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Transport of Acetic Acid in Polyethylene

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Polymer Science and Standards Division
Washington, DC 20234

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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BY

Joseph C. Phillips

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ABSTRACT

This report describes the mass loss and sorption/desorption of Acetic Acid (HAc) in polyethylene of different densities at various temperatures. Mass loss for a mixture of HAc and H₂O of three concentrations were also done at the highest temperature used.

Experimental data for mass loss were obtained at temperatures of 40 °C, 60 °C, and 78 °C for a conventional density bottle (CPE, $\rho \sim .92 \text{ g/cm}^3$) and a linear polyethylene density bottle (LPE, $\rho \sim .94 \text{ g/cm}^3$). At $t = 78 \text{ °C}$ a mixture of HAc/H₂O consisting of 100% HAc, 75% HAc, and 25% HAc by volume was used as permeant in the CPE and LPE bottles. From the mass loss data, the loss rate and diffusivity were determined.

Data for sorption/desorption were obtained at temperatures of approximately 30 °C, 50 °C, and 70 °C at a vapor pressure of $p = 17 \text{ mm Hg}$ (2.3 kPa). The low density polyethylene film (LDPE) had a density of $\rho \sim .906 \text{ g/cm}^3$ and a thickness of $10.16 \times 10^{-3} \text{ cm}$. From the sorption and desorption measurements, diffusivity, solubility, and permeability were determined.

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Introduction

Polymeric materials of low permeability are increasingly used as liners for storage and disposal of hazardous and municipal wastes. The primary function of these barrier materials is to prevent leachate and liquid components in the waste from leaking from an impoundment and polluting groundwater. For permanent storage, such as in municipal landfills, the liner should be an effective barrier for an extended period of time. In the absence of actual experience on the long term performance of polymeric liners there exists the need for predictive methods based on accelerated test methodologies for estimating service life.

Liner materials may be subject to a variety of chemical substances that may adversely affect the performance of the liner by chemical degradation, swelling the polymer, and environmental stress cracking. Each of these factors can degrade mechanical properties and increase transport of substances through the liner. Mechanical properties of the liner could be degraded to such an extent that holes are developed permitting rapid transport of the impounded liquid or leachate.

The overall goal of the present program is to identify factors which limit the long term performance of barrier materials and to develop test protocols for evaluation of candidate materials.

In the present phase of the work the compatibility of liner materials with simple organic acids is investigated. The series acetic, butyric and isobutyric acids have been identified as the major organic constituents of leachate from municipal landfills with the most prevalent species being acetic acid. The initial phase of the investigation is concerned with the compatibility of polyethylenes with acetic acid. The second phase will address the activity of acetic acid as an environmental stress cracking agent and the compatibility of polyethylenes of the kind used as a liner materials with other organic acids.

The transport of vapors and gases through a given material is dependent on the density, thickness, and the compatibility of the material and the vapor or gas [1]. The transmission performance of some barrier materials may be predicted to reasonable accuracy in certain instances [2,3]. In other cases, additional experimental data may be necessary. This report is concerned primarily with the transport of acetic acid through polyethylene at various temperatures and may be useful in characterizing certain materials as prospective liners for landfills.

The mass loss and sorption/desorption of acetic acid (HAc) in polyethylene bottles and LDPE (low density polyethylene) film have been investigated. Mass loss data were obtained as a function of temperature in LDPE (low density) and HDPE (high density) bottles. At the highest temperature used mass loss was recorded for various mixtures of HAc/H₂O. The sorption/desorption data were also obtained as a function of temperature at a single pressure using a LDPE film.

The results from mass loss indicate that the activation energy of permeation is independent of density over the range investigated. The diffusivity from sorption data at $p = 17 \text{ mm Hg}$ (2.3 kPa) as a function of temperature shows deviations from diffusivity determined from mass loss; this suggests a concentration dependence which increases from vapor to liquid.

Material*

A. Permeants

Reagent glacial acetic acid (MCB Manufacturing Chemists, Inc.; Cincinnati, OH) and distilled water were the liquids used. The acetic acid was used without further purification.

*Certain commercial equipment, instruments, or materials are identified in this report in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

B. Polyethylene

For mass loss measurements, conventional 125 ml polyethylene bottles ($\rho = .92 \text{ g/cm}^3$; also designated as CPE) and linear polyethylene bottles ($\rho = .94 \text{ g/cm}^3$; also designated as LPE) were used [4]. The actual densities as determined by a floatation method using ethanol/distilled water at 25 °C [4], were found to be, respectively, $\rho = .9235 \text{ g/cm}^3$ and $\rho = .9430 \text{ g/cm}^3$. The mean wall thickness of the CPE and LPE bottles were, respectively, .1062 and .0950 cm [4].

The sorption/desorption experiments were performed on low density PE film ($\rho = .906 \text{ g/cm}^3$; Abar Plastics, Inc., Beltsville, MD) with a thickness of .102 mm. The crystallinity determined from density measurements was 38.5% [comparatively, the crystallinities for the CPE and LPE bottles were, respectively, 47.3% and 59.5%].

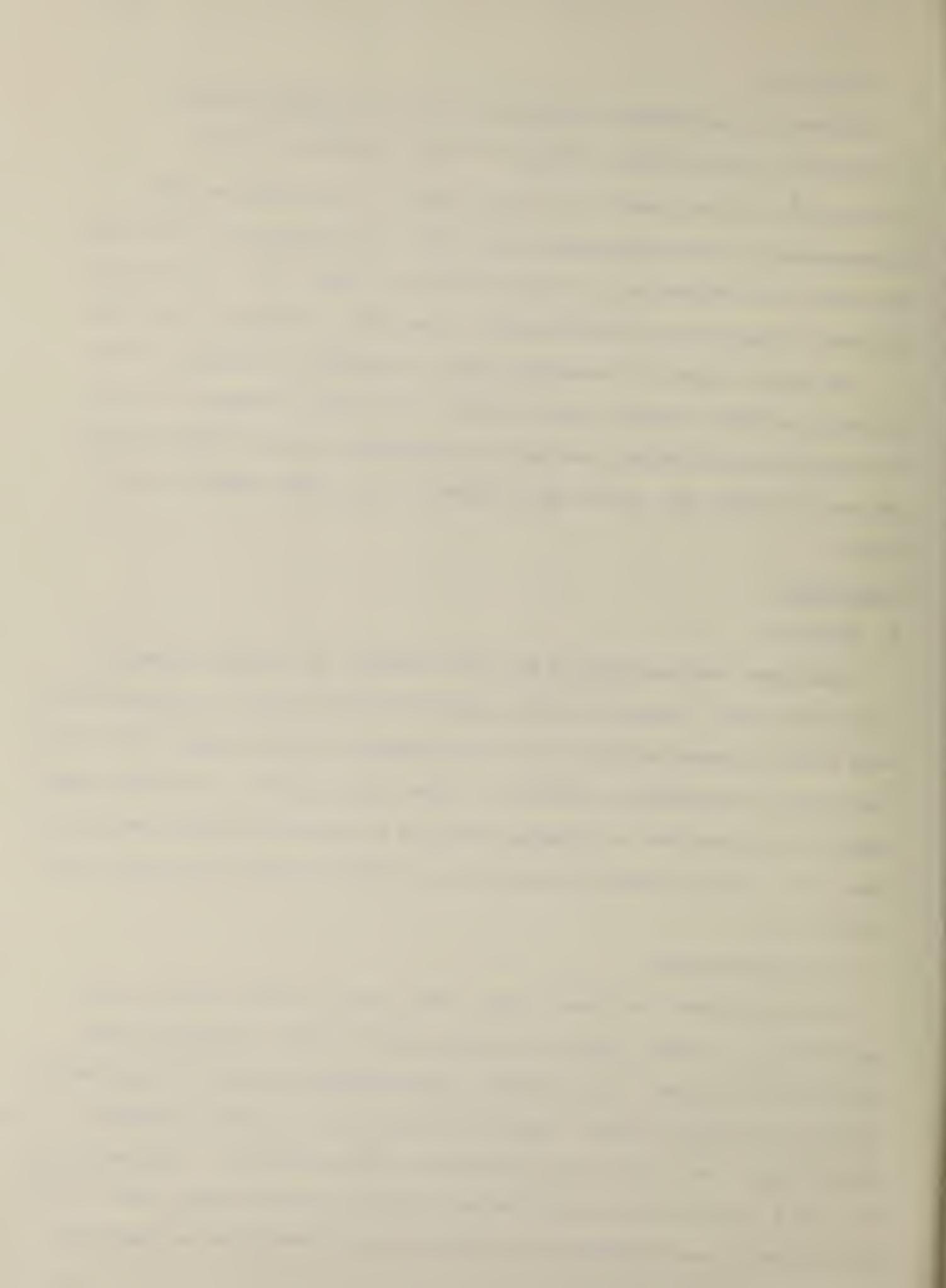
Experimental

A. Mass Loss

Experiments were performed at 40°C, 60°C and 78°C in a safety-designed air circulating oven. The sample bottles containing 100 ml of HA_C or HA_C/H₂O mixtures were placed on prescribed spaces within the oven that were calibrated with a quartz thermometer for temperature variations. After placing samples in the oven, weight determinations were done at subsequent times on a top-loading balance sensitive to about .01g. The loss rate for each bottle was determined from the change in mass versus time.

B. Sorption/Desorption

These experiments were done at 30°C, 50°C, and 70°C using a quartz spring sensitive to 2.7 mm/mg. Before performing each experiment, all samples were conditioned in vacuum. At a given time, the suspended rectangular sample (weight -49 mg) was allowed to come in contact with acetic acid vapor at a pressure $p = 17 \text{ mm Hg}$ (2.3 kPa). From a plot of the reduced mass uptake $[M(t)/M(\infty) = \text{the mass uptake at time } t \text{ divided by the equilibrium mass uptake}]$ versus the square root of time, the diffusivity was determined; the solubility was obtained from the equilibrium mass uptake $[M(\infty)]$.



Results and Discussion

A. Mass Loss

Figures 1 and 2 show mass loss for the LDPE and HDPE bottles for temperatures of 40 °C and 60 °C, respectively. At $t = 78$ °C mass loss measurements were performed for various concentrations of acetic acid in distilled water as shown in Figure 3 for the LDPE bottles and in Figure 4 for HDPE bottles. The concentrations of acetic acid in volume percent were 100%, 75%, 50% and 25%. All of the curves as shown possess the same general mass loss-time behavior, i.e., beyond the induction period, the curves approach linear behavior asymptotically. From permeation theory [5], such behavior may be represented as

$$\Delta m = \dot{Q} (t - \underline{q}(t/\tau)\tau) \quad (1)$$

where Δm is the mass loss at time t , \dot{Q} is the steady-state rate of loss, \underline{q} describes the molecular transport process and initial experimental conditions, and τ is the time-lag which is proportional to the thickness of the container wall, λ , and inversely proportional to the diffusivity of the permeant, D , i.e.,

$$\tau = \lambda^2/6D \quad (2)$$

The parameter \underline{q} may be calculated [6] if certain assumptions are made concerning the initial state of the polymer, the Fickian nature of the transport process, and the concentration independence of the diffusion constant.

The steady-state loss rate determined from the mass loss data is shown in Fig. 5 for the CPE and LPE bottles as a function of temperature. The $\log \dot{Q}$ versus reciprocal temperature plots are linear and parallel. This indicates that the activation energy, E_p , for permeation is approximately constant for both CPE and LPE bottles, i.e.,

$$\dot{Q} = \dot{Q}_0 e^{-E_p/RT} \quad (3)$$

The value for E_p over the temperature range shown in Fig. 5 was found to be 17.3 Kcal/mole. This value compares rather well with E_p calculated from the data of

Salame [3] for acetic acid in PE. The quantity \dot{Q}_0 may be estimated for CPE and LPE by extrapolating the data in Fig. 5 to $1/T = 0$. By inserting the results of Eq. (3) into Eq. (1), the amount of permeant lost as a function of time may also be determined.

The uncertainty in the calculation of D using Eq. (2) depends dramatically on the uncertainty in time lag τ and the thickness ℓ . The former quantity may vary from a few percent to well over 100% depending on whether the equilibrium loss rate had been attained over the time range of measurement; the latter quantity contributes an uncertainty that varies as the square of the thickness and may be substantial for very thin and/or inhomogeneous walls [e.g., the error in ℓ ranged from $\pm 7\%$ for the LPE bottles to $\pm 18\%$ for the CPE bottles].

In order to test the influence of a second component on the loss rate of acetic acid measurements were made at various concentrations in distilled water. The results in terms of volume fraction of acetic acid, V , are shown in Figure 6. A plot of $\log \dot{Q}$ versus V was non-linear while a plot of $\log \dot{Q}$ versus V^α was linear, i.e.,

$$\log \dot{Q} = \log \dot{Q}_0 + V^\alpha \quad (4)$$

where α is a constant and was found to be roughly 2.5. The rationale for the behavior exhibited by Eq. (4) has not been explored at this time. It may be noteworthy to mention that a simple additivity concept [6] using the mole fractions of components 1 and 2 doesn't seem to apply to the $\text{HA}_C/\text{H}_2\text{O}$ mixtures for the concentration range used here. Apparently one can not neglect the different kinds of interactions that exist in this system, e.g., polymer/liquid [PE/ HA_C , PE/ H_2O , PE/ $\text{HA}_C:\text{H}_2\text{O}$] and liquid/liquid ($\text{HA}_C/\text{H}_2\text{O}$, HA_C/HA_C , $\text{H}_2\text{O}/\text{H}_2\text{O}$).

B. Sorption/Desorption

The sorption and desorption of acetic acid vapor at $p = 17$ mm (2.3 kPa) for $t = 30$ °C, 50 °C, and 70 °C are shown in Figures 7, 8, and 9 respectively. The behavior at very early times could be Fickian while the increasing differences between sorption and desorption curves suggest a concentration-dependent diffusion constant. The limiting diffusivity constant, D , was calculated from the reduced mass uptake as $t \rightarrow 0$ [7], i.e.,

$$M(t)/M(\infty) = 2/\lambda (4D/\pi)^{1/2} t^{1/2} \quad (5)$$

where $M(t)$ is the mass uptake at time t and $M(\infty)$ is the equilibrium mass uptake at $t \rightarrow \infty$. The equilibrium mass uptake and concentration at 30°C, 50°C and 70°C are, respectively, $M(\infty)=0.344$ mg, $c=7.02 \times 10^{-3}$ mg/mg; $M(\infty)=0.122$ mg, $c=2.49 \times 10^{-3}$ mg/mg; and $M(\infty)=0.047$ mg, $c=8.28 \times 10^{-4}$ mg/mg. The solubilities at $p=17$ mm Hg were calculated from the concentrations, i.e., $S=c/p$ where $c=M(\infty)/M_f$ is the ratio of the equilibrium mass uptake to the mass of the film ($M_f \sim 49$ mg]. Due to spring oscillation, data for times earlier than shown was difficult to obtain. The desorption and sorption data appears to be as expected at all three temperatures, i.e., the slope of the reduced mass uptake versus $t^{1/2}$ tends to increase with temperature which indicates a corresponding increase in diffusivity.

The diffusivity and solubility determined from sorption as a function of temperature are shown in Figure 10. The apparent linear relationships suggest that the activation energy of diffusion, E_D , and the heat of solution, ΔH , are roughly constant over the temperature range investigated, i.e.,

$$D = D_0 e^{-E_D/RT} \quad (6)$$

or

$$S = S_0 e^{-\Delta H/RT}$$

The values determined for E_D and ΔH were, respectively, 11.1 Kcal/mole and -11.3 Kcal/mole. The heat of solution, ΔH , suggest that the heat of condensation is negative and greater in magnitude than the heat of mixing, i.e., $\Delta H = H_{\text{cond}} + H_{\text{mix}}$. The term H_{cond} depends on the Lennard-Jones potential parameter, ϵ/\bar{k} , which is quite dependent on permeant size and polarity [8]. The term H_{mix} is a function of the mixing parameter χ [8]. In addition to the two terms mentioned above, ΔH also has a contribution due to any crystalline melting that may occur over the temperature range of interest.

The calculated permeability [$P=SD$] from Fig. 10 shows little temperature dependence for sorption which seems to be in agreement with that determined from E_p , i.e., $P=P_0 e^{-E_p/RT}$ where E_p may be estimated from E_D and ΔH [$E_p = \Delta H + E_D$].

If one assumes that $E_D \sim H_{\text{cond}}$, then it is apparent that H_{mix} makes a small almost negligible contribution to the overall activation energy of permeation for HA_c in the sorption experiment using thin films of LDPE. Also shown in Fig. 10 are calculated values of the diffusivity determined from the mass loss data utilizing Eq. (2); the density and thickness were those of LDPE films used for the sorption/desorption measurements. The difference in the sorption and mass loss results seems to suggest that the diffusivity is concentration-dependent. This explanation seems to be reasonable since the sorption measurements were performed at a low vapor pressure ($p=17$ mm Hg) while mass loss measurements were done with liquid. To further check the diffusivity results in Fig. 10, it would be desirable to obtain mass loss from a lower density bottle and to perform sorption/desorption measurements as a function of pressure.

Conclusion

This preliminary investigation has presented data at various temperatures on mass loss and sorption/desorption of acetic acid in PE bottles and LDPE films. From the mass loss measurements, loss rate and diffusivity were determined; from the sorption/desorption data, diffusivity and solubility were calculated. The temperature dependence of these properties indicate that activation energies of permeation and diffusion and the heat of solution are roughly constant over the temperature ranges investigated. Differences in sorption and desorption results and the comparison of diffusivity calculated from mass loss measurements also suggest that diffusivity is concentration-dependent.

This investigation also attempted to address the question of mixtures. Even though HAC/H₂O solutions were studied only at one temperature, the effect of adding H₂O to HAC can dramatically affect the loss rate of HAC. It would be highly desirable to study this mixture and other mixtures of different acids in the homologous series as a function of temperature. Such a study would be of great benefit in helping to characterize a given plastic as a potential liner material.

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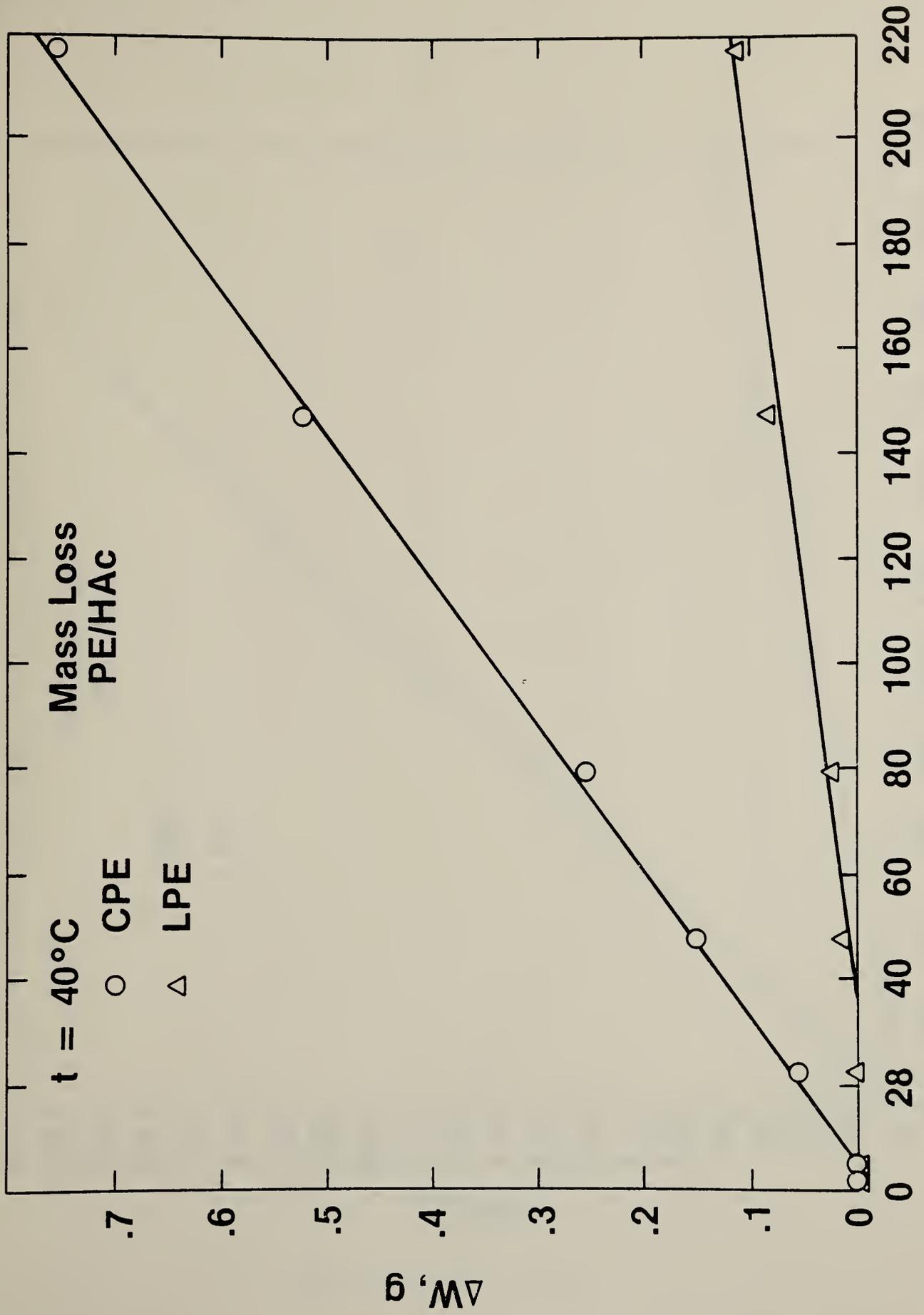


Fig. 1

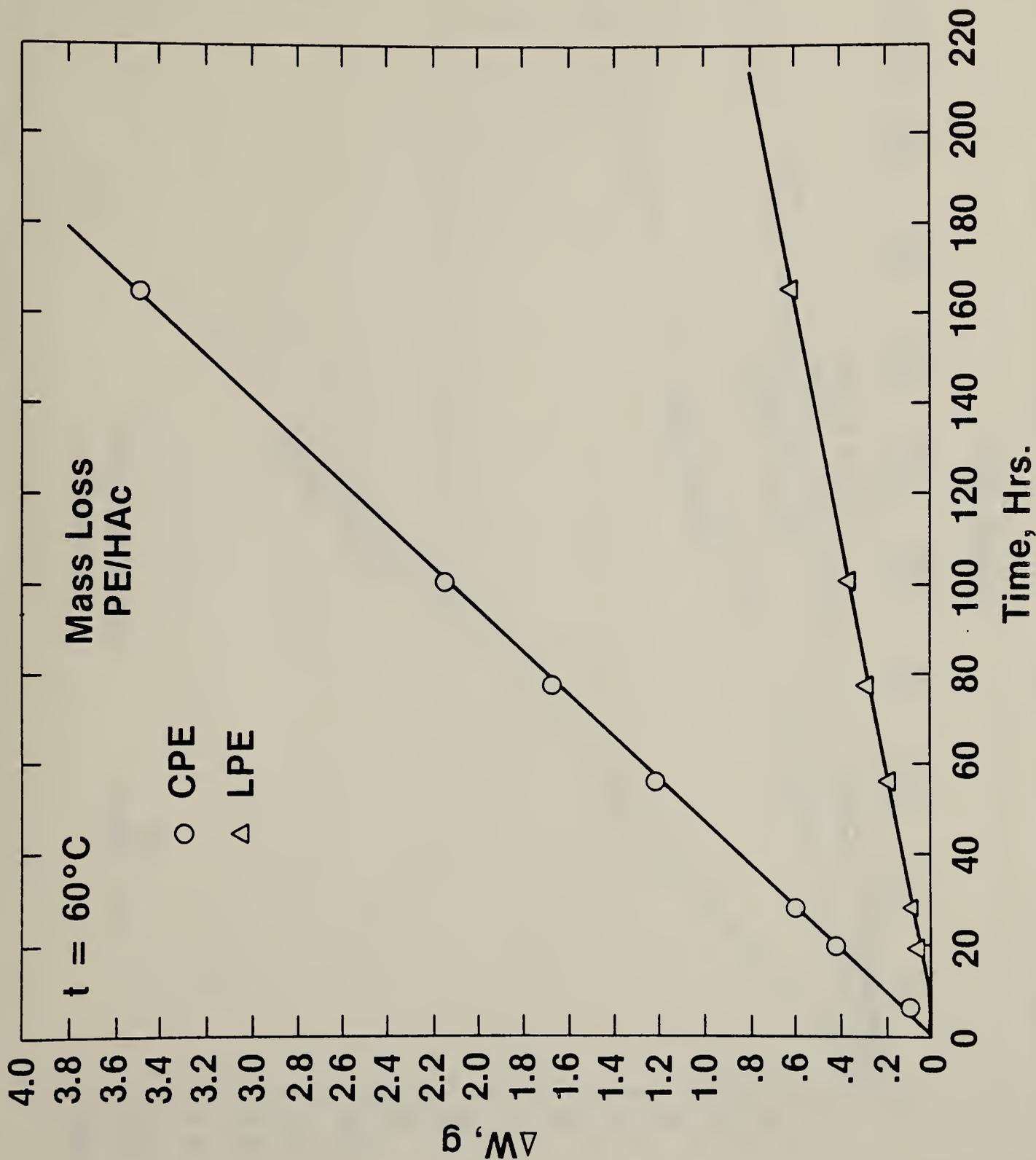


Fig. 2

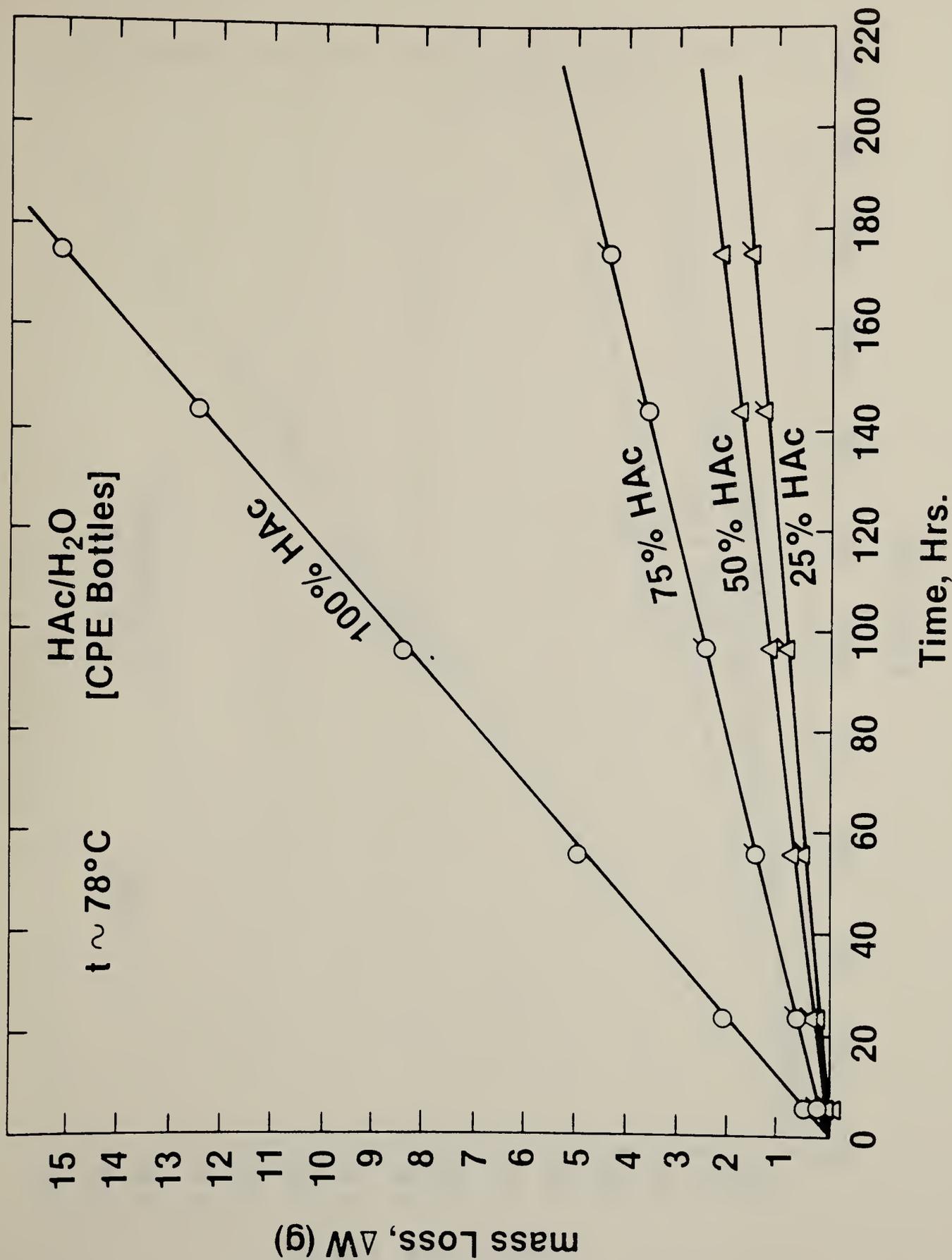


FIG. 3

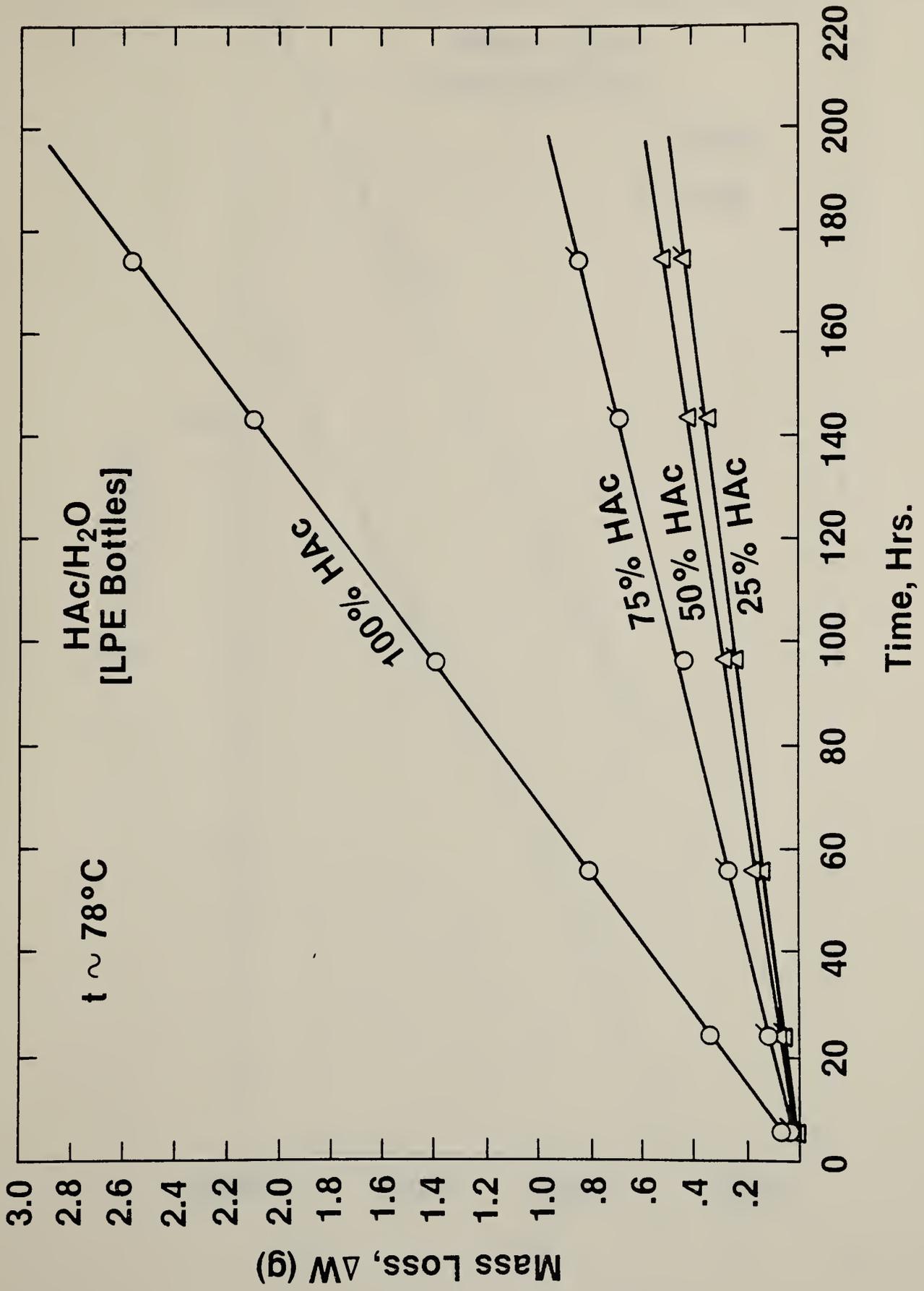


Fig. 4

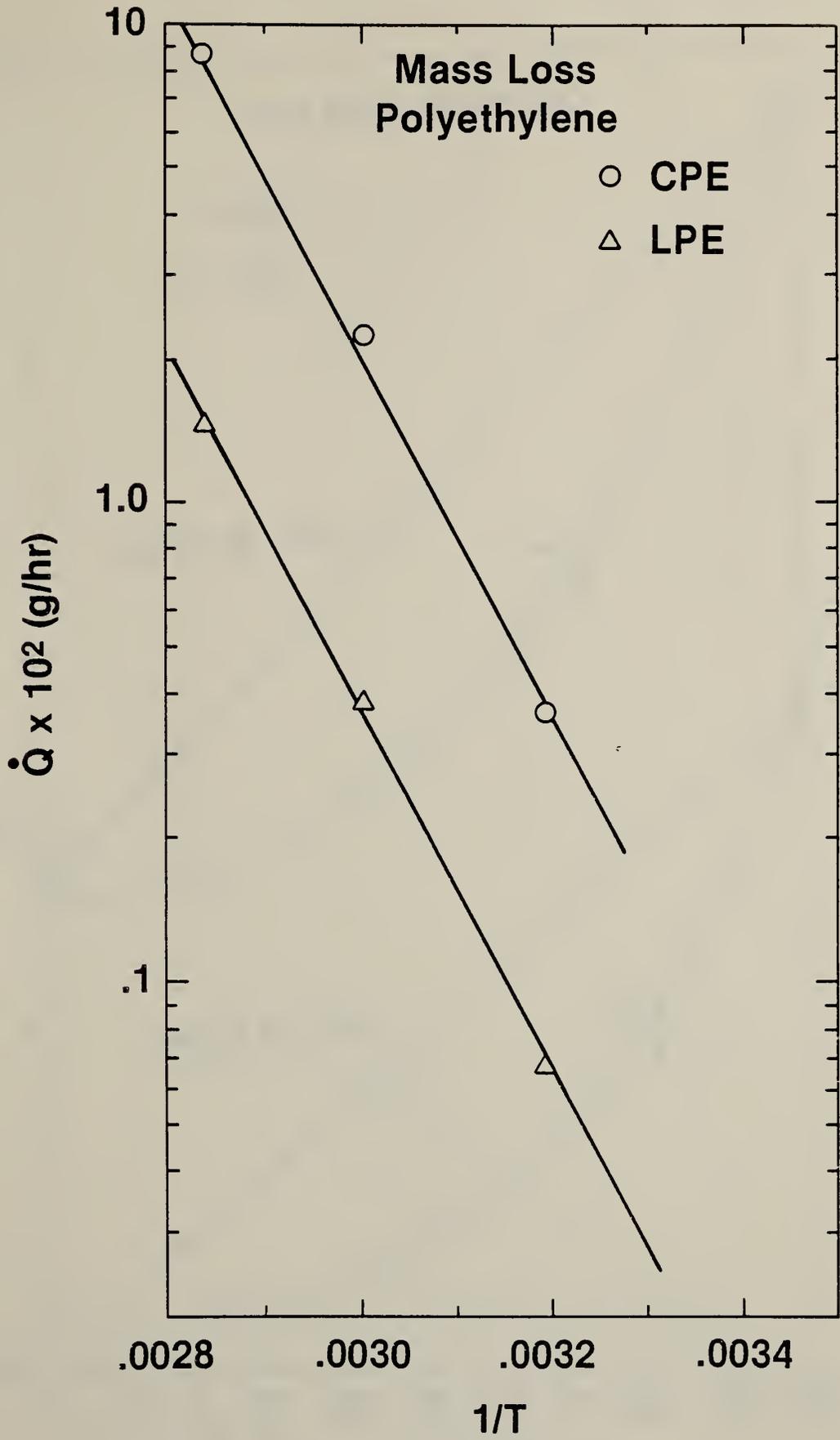


Fig. 5

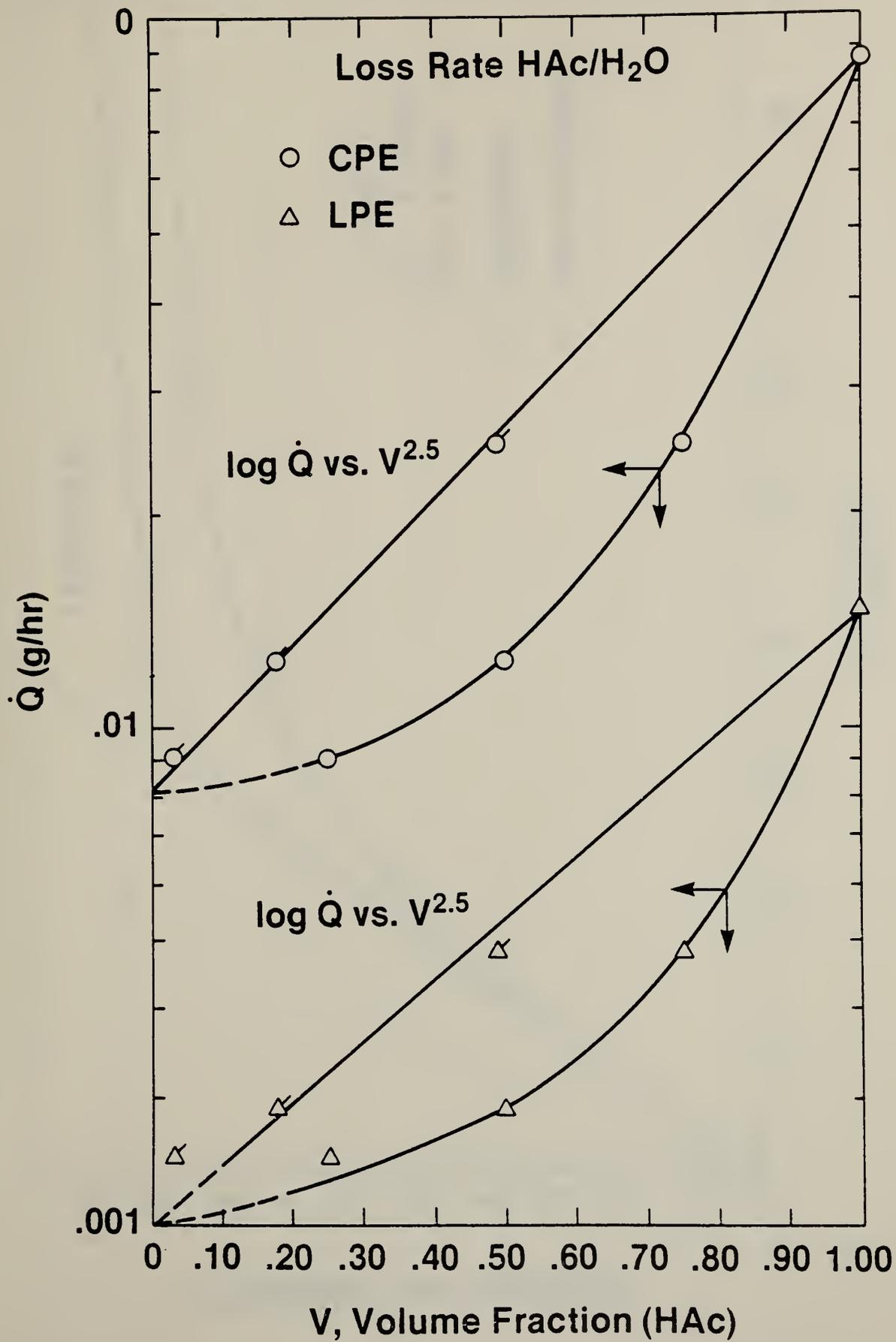


Fig. 6

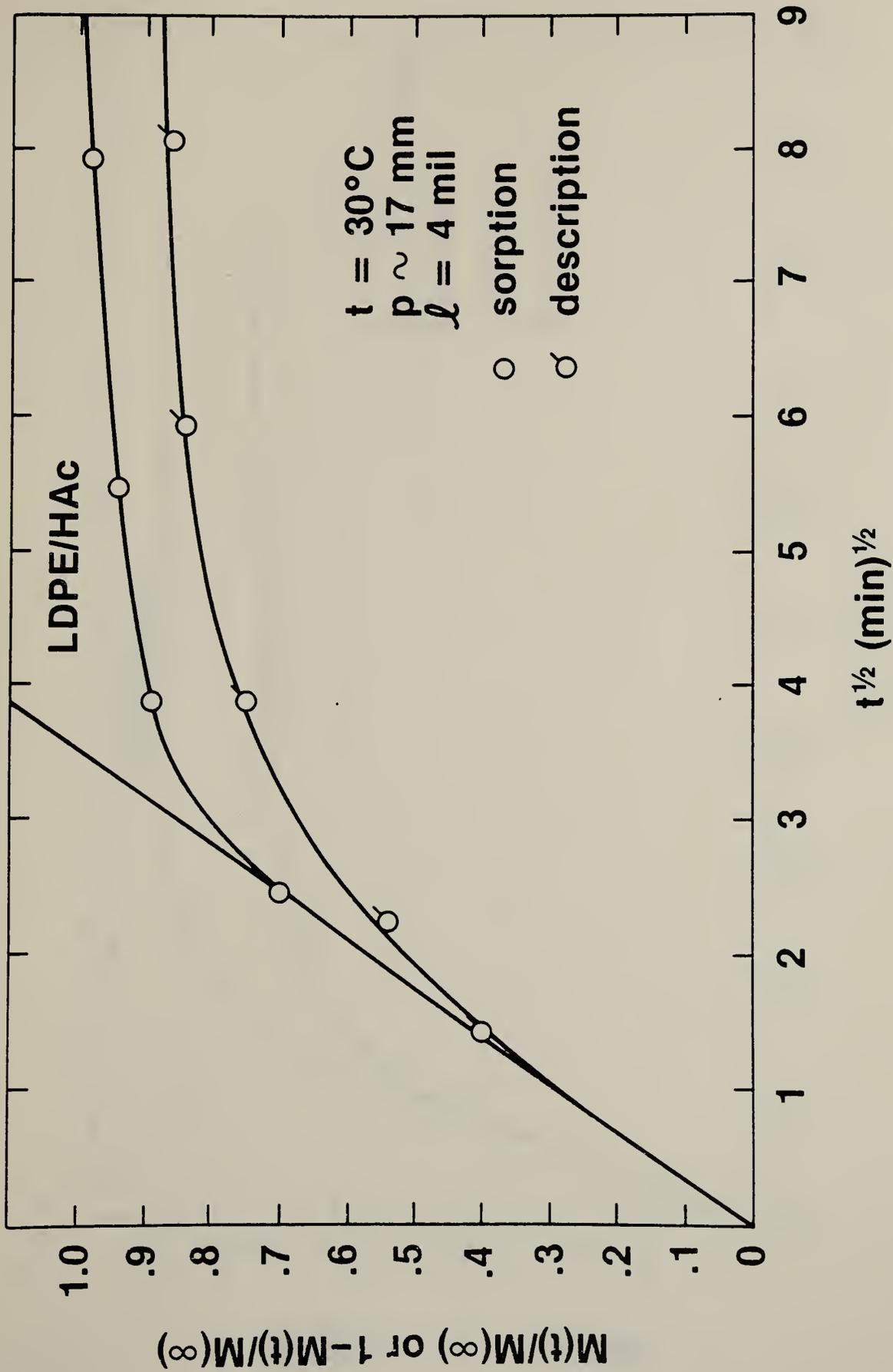


Fig. 7

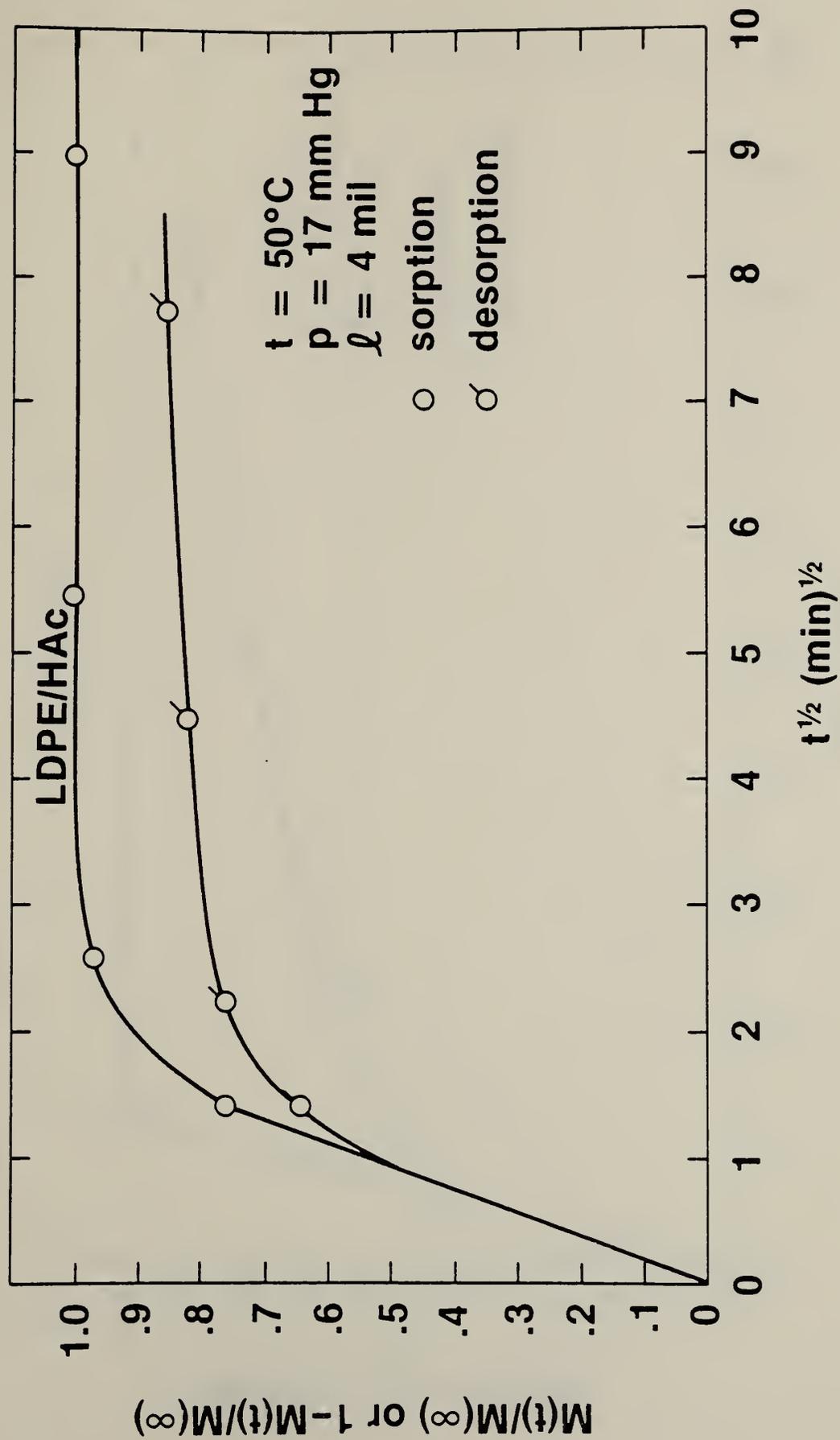


Fig. 8

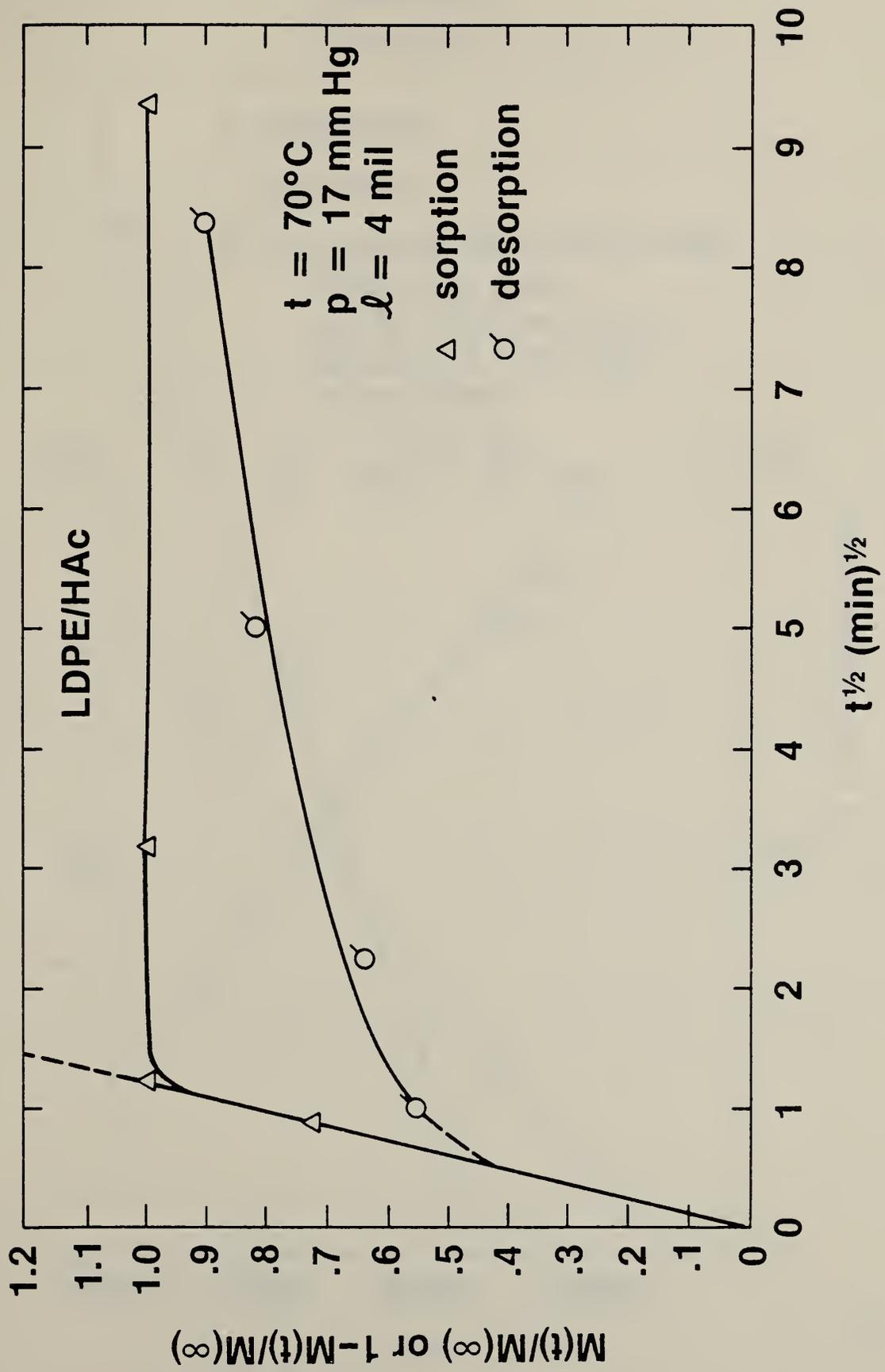


Fig. 9

LDPE/HAc
(Sorption)

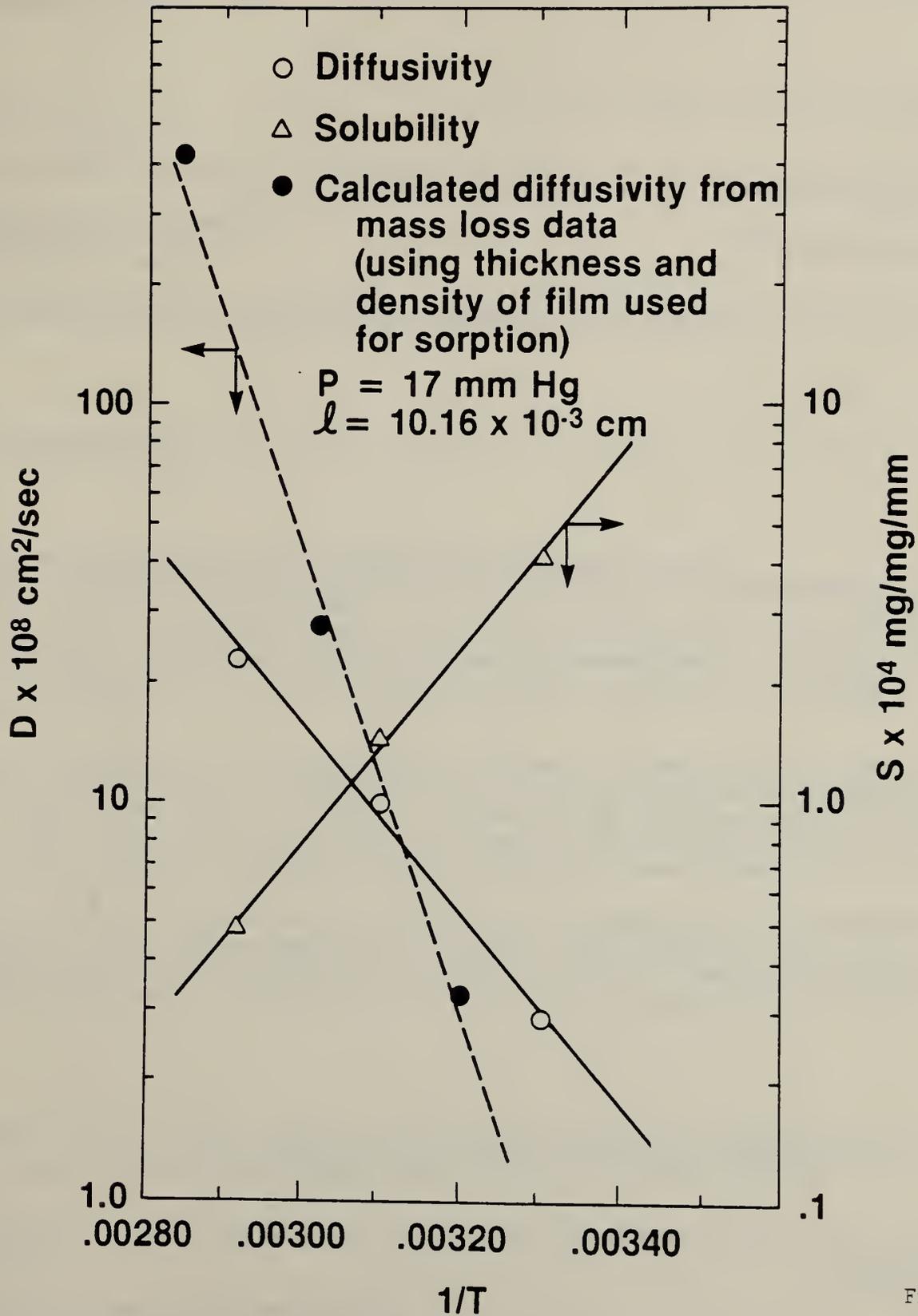


Fig. 10

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11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> <p>This report describes the mass loss and sorption/desorption of Acetic Acid (HAc) in polyethylene of different densities at various temperatures. Mass loss for a mixture of HAc and H₂O of three concentrations were also done at the highest temperature used.</p> <p>Experimental data for mass loss were obtained at temperatures of approximately 40°C, 60°C, and 78°C for a low density bottle (LDPE, $\rho \sim .92 \text{ g/cm}^3$) and a high density bottle (HDPE, $\rho \sim .94 \text{ g/cm}^3$). At $t=78^\circ\text{C}$ a mixture of HAc/H₂O consisting of 100% HAc, 75% HAc, and 25% HAc by volume was used as permeant in the LDPE and HDPE bottles. From the mass loss data, the loss rate and diffusivity were determined.</p> <p>Data for sorption/desorption were obtained at temperatures of approximately 30°C, 50°C, and 70°C at a vapor pressure of $\rho \sim 17 \text{ mm Hg}$. The polyethylene film had a density of $\rho \sim .906 \text{ g/cm}^3$ and a thickness of 4 mil ($10.16 \times 10^{-3} \text{ cm}$). From the sorption and desorption measurements, diffusivity, solubility, and permeability were determined.</p>			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> Acetic Acid, desorption, diffusion, mass loss, polyethylene, sorption.			
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